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By H. C. Biddle.

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THE REDUCTION OF COPPER BY SOLUTIONS OF FERROUS SALTS.

BY H. C. BIDDLE.

The genesis of the great deposits of native copper is a subject which has invited considerable attention. The commonly accepted theory that the copper has been deposited from its compounds by solutions of ferrous salts is based on the close relation between the reduced metal and the ferric oxide contained in the associated minerals.¹ It is consequently of interest to determine experimentally under what conditions such reduction may occur. Some investigation has already been conducted in this direction.

As early as 1861 Knop succeeded in forming cuprous hydroxide by treating a mixture of cupric and ferrous sulphates with alkaline carbonate.² In one instance he speaks of obtaining traces of copper. In 1864 Wibel repeated Knop's experiments,³ but was unable to verify the latter's statement re-

¹ Raphael Pumpelly: *Am. J. Sci.*, **2**, 353 (1871); R. D. Irving: *Mon. U. S. Geol. Surv.*, No. 5, p. 420 (1883).

² A. Knop: *N. Jahrb. für Min.*, (1861), p. 513.

³ Ferd. Wibel: "Das Gediegen-Kupfer und das Rothkupfererz," (1864), p. 20.

garding the reduction to metallic copper. When, however, a mixture of ferrous and cupric hydroxides, formed by adding potassium hydroxide to a solution of the sulphates, was heated to 210° C., traces of copper were obtained. Solutions of the sulphates and coarsely powdered wollastonite, subjected to the same treatment, yielded a like result. The separation of metal, however, was slight and the part played by the ferrous hydroxide in the reduction was, at the time, somewhat questioned.

In 1867 Braun observed the partial deposition of copper from a mixture of ferrous and cupric salts when these were dissolved in large excess of ammonium carbonate.¹ The same year Weith secured a ready reduction in the presence of tartaric acid.²

He failed to note, however, that under the same conditions the organic acid itself will slowly reduce the copper salts. A mixture of calcium hydroxide with a solution of ferrous and cupric sulphates, was allowed to stand for several weeks. The precipitate thus obtained, when treated with acetic acid, left a residue of cuprous oxide and copper. Strangely enough, Weith overlooked the fact that cuprous oxide with acetic acid yields cupric acetate and metallic copper. In 1869 Hunt³ stated that copper could be obtained by the action of cupric chloride on freshly precipitated ferrous hydroxide, or carbonate. Nothing is given, however, to indicate that the metal was actually detected by isolating it from ferric hydroxide precipitated along with it.

The deposition of copper by solutions of ferrous salts is a reversible reaction governed by the ordinary laws of chemical equilibrium.

It is to Arrhenius largely that we owe the view that certain substances in solution are more or less dissociated into electrically charged parts, or ions. This theory has proved of the highest value in affording an insight into the principles of chemical reactions. Different substances differ much in their tendency to pass into the ionic form, and this ten-

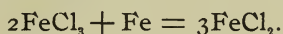
¹ E. Braun: *Ztschr. Chem.*, (1867), p. 569.

² W. Weith: *Ibid.*, (1867), p. 623.

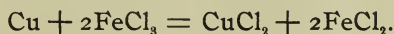
³ Sterry Hunt: *Compt. rend.*, (1869), p. 1357.

dency is greatly influenced by external conditions, particularly by the nature of the solvent. The chief source of ions is the dissociation of electrically neutral molecules such as occurs in the aqueous solutions of salts, acids, and bases. They may further be formed from electrically neutral substances which enter the ionic condition by partially, or wholly, appropriating the electric charge of ions already present.¹

As an example of this mode of formation may be mentioned the reduction of ferric salts by the action of metallic iron :

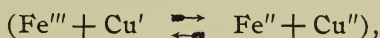


The solution of metallic copper in ferric chloride is an action of the same nature :



As is seen, the deposition of copper by a ferrous salt would be the reverse of this last reaction.

The conditions under which such reduction should occur may be readily determined. In a system which contains a solution of iron and cupric salts in contact with metallic copper, and in which the several constituents have attained a constant value, a condition of equilibrium subsists, on the one hand, between ferric, cuprous, ferrous, and cupric ions



and, on the other hand, between ferric, ferrous, and cuprous ions, and the active mass of the metallic copper



If a , b , c , d , respectively, represent the active masses of the ions in the first instance, an equation of equilibrium may be thus formulated : $\frac{a \cdot b}{c \cdot d} = K$.² The active mass of the copper is of constant value, hence in the second instance, retaining the same letters, we have the expression $\frac{a}{b \cdot c} = K'$.

¹ F. W. Küster : Ztschr. Elektrochem., 4, 105.

² W. Nernst : "Theoret. Chem.," p. 358.

The precipitation of copper would then be favored by increasing the concentration of ferrous, cuprous, and cupric ions and by decreasing that of the ferric ions.

The deposition of the metal, consequently, should depend on the relative active masses of the ions present.

This assumption is fully sustained by the experimental evidence which follows :

The precipitation of metallic copper by solutions of ferrous salts is a reversible action, whose direction in any case is determined by the relative concentration of the ferrous, ferric, and copper (cuprous and cupric) ions.

(a) In a solution containing an appreciable quantity of ferric ions, or in which these would be formed in the course of the reaction, metallic copper will not be deposited.

This is shown in the inability of ferrous chloride, or sulphate, to reduce corresponding copper salts, even though the mixed solutions stand for an indefinite period. This inaction is, indeed, to be expected when we consider that solutions of ferric salts, as the sulphate and chloride, easily dissolve metallic copper with the formation of a cupric salt.

From this it is readily understood why Wibell¹ obtained no reduction of the copper salts on heating the mixed sulphates together to 210° C. in solution.

(b) In a solution containing few ferric ions, and in which the reaction does not result in their appreciable increase, a sufficient concentration of ferrous and copper ions will result in the deposition of metallic copper.

The tendency of ferrous to reduce copper salts is shown in the precipitation of cuprous sulphocyanate by the action of the ammonium salt on a solution of ferrous and cupric chlorides. The same tendency appears in the formation of cuprous chloride on treating cupric oxide with a solution of ferrous chloride.² From an emulsion of ferrous and cupric hydroxides, after long standing, crystals of cuprous oxide can be separated. That further reduction is largely determined by the concentration of the cupric and ferrous ions, appears prob-

¹ "Das Gediengen-Kupfer und das Rothkupfererz," p. 20.

² Sterry Hunt: *Loc. cit.*

able from the action of ammonium carbonate on a solution of ferrous and cupric chloride.¹

The precipitate first formed on adding the carbonate to the mixed chlorides dissolves in an excess of the precipitant to a yellow liquid, from which, on standing twenty-four hours, a slight but brilliant mirror of metallic copper is deposited on the walls of the vessel.

The influence of the concentration of the ions on the reduction of copper is clearly shown in the behavior of the mixed carbonates under varying conditions.

When a solution of cupric and ferrous chlorides (1 mol. CuCl_2 : 2 mol. FeCl_2) is added to a considerable excess of sodium carbonate, a greenish precipitate of the carbonates is obtained, which undergoes but slight change on standing. Such a solution, indeed, would naturally little favor the separation of metallic copper, since the highly ionized alkaline carbonate would greatly decrease the active masses of the ferrous and ferric ions.

If the alkaline carbonate employed is only slightly in excess of that required to precipitate the copper and iron salts, the concentration of the carbonic acid ions will be greatly diminished. Under these more favorable conditions reduction slowly takes place with loss of carbon dioxide. The carbonates gradually change to a brick-red precipitate containing metallic copper and basic ferric carbonate.

As is well known, the acid ferrous and cupric carbonates are more soluble than the corresponding normal or basic salts of these metals. The influence of this greater solubility is shown in the precipitation of small amounts of copper even in the presence of a large excess of alkaline bicarbonates. If the metallic chlorides are added to a saturated solution of acid potassium carbonate and the mixture allowed to stand for twenty-four hours, a slight film of metallic copper, mixed with basic ferric carbonate, is deposited on the walls of the vessel.

The solubility of the acid carbonates of iron and copper is largely increased under pressure.² The greater concentration

¹ E. Braun : *Loc. cit.*

² R. Wagner : *Ztschr. anal. Chem.*, 6, 167.

of the metallic ions thus obtained produces a ready reduction of copper even in the presence of concentrated solutions of the acid alkaline carbonates.

A tube containing a solution of ferrous and cupric chlorides is placed in a thick-walled flask holding a saturated solution of potassium bicarbonate. The flask is then filled with carbon dioxide, tightly sealed, and the contents of the tube mixed with the alkaline bicarbonate. The precipitate formed gradually loses carbonic acid, finally assuming the brick-red color already noted. The supernatant ruddy liquid owes its color to the presence of some basic ferric carbonate, which is deposited when the solution is warmed, as ferric hydroxide. The precipitate contains finely divided copper, which cannot readily be freed from the intimately associated ferric iron by treatment with hydrochloric acid, because of the solvent action of ferric chloride, but on digesting the original mixture a short time a coagulum is usually formed, from which, by repeated agitation with water, the heavier metal is separated.

The copper thus obtained is of characteristic appearance, is insoluble in hydrochloric acid, but soluble in nitric, the solution showing the presence of copper and absence of iron.

The reduction of copper from the cuprous condition may be effected in the same manner as from the cupric. This is readily shown by substituting for the cupric salt, in the above reaction, cuprous chloride dissolved in a solution of sodium chloride. From one gram of cuprous chloride more than half of the metal can thus be easily isolated as pure copper, free from ferric iron.

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